



Comparative Study between Nanofiltration and Reverse Osmosis Membranes for the Removal of Heavy Metals from Electroplating Wastewater

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ABSTRACT

The present work aimed to study the efficiency of nanofiltration (NF) and reverse osmosis (RO) process for water recovery from electroplating wastewater and study the factors affecting the performance of two membrane processes. Nanofiltration and reverse osmosis membranes are made from polyamide as spiral wound module. The inorganic materials $ZnCl_2$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$ were used as feed solutions. The operating parameters studied were: operating time, feed concentrations for heavy metal ions, operating pressure, feed flow rate, feed temperature and feed pH. The experimental results showed, the permeate concentration increased and water flux decreased with increase in time from 0 to 70 min. The permeate concentrations increased and flux decreased with increase in feed concentrations from 10 to 300 mg/l. Raising of pressure from 1 to 4 bar, permeate concentration decreased for RO, for NF decreased and then increased at high pressure and increase the flux. The rises of flow rate from 20 to 50 l/h decreased permeate concentration and the flux increase. The rises of temperature from 26 to 40 °C, increased permeate concentration and increased the flux. The rise in pH from 4 to 7, decreased the flux as the pH goes from acidic side towards alkaline. The polyamide nanofiltration membrane had allowed permeation of chromium and copper ions to lower than permissible limits. Nanofiltration membrane had allowed permeation of nickel and zinc ions at low concentration of these ions. The polyamide RO membrane gave a high efficiency for removal of chromium, copper, nickel and zinc and it had allowed permeation of these ions to the lower than permissible limits. The rejection at first three minutes when the feed concentration approximately was constant for chromium in NF and RO, was 99.7% and 99.93%, for copper was 98.43% and 99.33%, for zinc was 97.96% and 99.49%, and for nickel was 97.18% and 99.49% respectively. The maximum recovery for chromium in NF and RO was 71.75% and 48.5%, for copper was 75.62% and 50.68%, for zinc was 80.87% and 54.56%, for nickel was 60.06% and 46.18% respectively. For a mixture of synthetic electroplating wastewater, nanofiltration and reverse osmosis membranes have a high rejection percentage for heavy metal ions. It was obtained pure water and concentrations of less than allowable limits for heavy metals in the case of the mixture.

Key words: nanofiltration, reverse osmosis, electroplating wastewater.

دراسة مقارنة بين اغشية النانو والتناضح العكسي لإزالة المعادن الثقيلة من مياه الصرف الصحي الناتجة من الطلاء الكهربائي

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الخلاصة

هذا العمل يهدف إلى دراسة كفاءة غشاء النانو وعملية التناضح العكسي لاسترجاع المياه من مياه الصرف الصحي الناتجة من الطلاء الكهربائي، ودراسة العوامل التي تؤثر في أداء الغشائين. اغشية النانو والتناضح العكسي مصنوعة من مادة البولي أميد

على شكل (spiral wound module). المواد غير العضوية كانت كلوريد الزنك، كلوريد النحاس المائي، كلوريد النيكل المائي، و كلوريد الكروم المائي استخدمت ك محلول للقيم. العوامل التشغيلية التي تم دراستها هي: الزمن، تركيز الداخل، الضغط، التدفق، درجة الحرارة، درجة الحموضة. وأظهرت النتائج التجريبية، تركيز الناتج يزداد و تدفق المياه يقل مع زيادة الوقت (0-70 دقيقة). تركيز الناتج يزداد و تدفق المياه يقل مع زيادة تركيز الداخل (10-300) ملغ/لتر. رفع الضغط (1-4 بار)، تركيز الناتج يقل للتناضح العكسي ويقل ثم يزداد عند الضغط العالي لغشاء النانو ويزداد تدفق المياه. رفع التدفق (20-50 لتر/ساعة)، يقل تركيز الناتج ويزداد الجريان. رفع درجة الحرارة (26-40 درجة مئوية)، يزداد تركيز الناتج ويزداد الجريان. رفع درجة الحموضة (4-7)، يقل الجريان كلما يذهب الرقم الهيدروجيني من الجانب الحمضية نحو القلوية. غشاء بولي أميد NF أتاح تخلل أيونات الكروم والنحاس إلى أقل من الحدود المسموح بها. NF أتاح تخلل أيونات النيكل والزنك إلى أقل من الحدود المسموح بها عندما تتواجد بتركيز منخفضة. غشاء بولي أميد RO يعطي كفاءة عالية لإزالة الكروم والنحاس والنيكل والزنك، وقد أتاح تخلل هذه الأيونات إلى أقل من الحدود المسموح بها. كان الرفض في ثلاث دقائق الأولى عندما كان تركيز التغذية ثابتا تقريبا للكروم في NF و RO 99.7% و 99.93%، للنحاس هو 98.43% و 99.33%، للزنك هو 97.96% و 99.49%، للنيكل 97.18% و 99.49% على التوالي. وكان الحد الأقصى لاسترداد الماء في حالة الكروم في NF و RO 48.5%، النحاس 75.62% و 50.68%، الزنك 80.87% و 54.56%، النيكل 60.06% و 46.18% على التوالي. لخليط من مياه الطلاء الكهربائي الاصطناعية، أغشية النانو والتناضح العكسي لديها نسبة الرفض عالية لأيونات المعادن الثقيلة. تم الحصول على مياه نقية وبتراكيز أقل من الحدود المسموح بها للمعادن الثقيلة في حالة الخليط. الكلمات الرئيسية: غشاء النانو، التناضح العكسي، مياه الصرف الصحي الناتجة من الطلاء الكهربائي.

1. INTRODUCTION

As the world's population and the consequent demand for water supply increase, the world is facing a fresh water crisis due to the rapid depletion of the resources of fresh water. Domestic and industrial activities have contaminated the ground water and the surface water to a large extent. Precious resource conservation and the sustainable development of water will require maximal recycling and reuse, **Alzahrani, et al., 2013 and Dannys, et al., 2016**. Due to discharge of big amounts of waste water contaminated with heavy metals, industries containing heavy metals, such as Cu, As, Cd, Ni, Cr, Zn and Pb; are the most dangerous among the chemical intensive industries. Heavy metals can be absorbed by living organisms, due to their high solubility in the aquatic environments. If the heavy metals are found beyond the permitted concentration limits, they can cause health problems, **Barakat, 2011**. Waste water contains the heavy metals originated from tanneries, batteries, pesticides galvanizing plants, fertilizer industries, metal plating facilities, mining operations, paper industries and pigment, stabilizers and thermoplastics manufacture and etc., **Jain, 2013**. The maximum contaminant level (standards) of zinc metal in water is <10 mg/l, **Wahaab, et al., 2010**, copper metal is 4 mg/l, nickel metal is 4 mg/l and chromium metal is 2 mg/l, **Abhang, et al., 2013**.

The wastewater from electroplating industry that is polluted with heavy metals attracted increasing interest due to the development of this industry in last years. The wastewater from electroplating consists of heavy metals such as cadmium, chromium, nickel, zinc and copper. However, the heavy metals and pure water have a great possibility of being reused if the heavy metals from wastewater of electroplating industry can be removed efficiently, **Wei, et al., 2013**. Various technologies have been applied for the removal of heavy metals from water and waste water, such as chemical precipitation, adsorption, coagulation-flocculation, floatation, ion exchange, electrochemical processes, and membrane filtration, **Boricha, and Murthy, 2009**. The techniques involving chemical reactions require the use of large amounts of expensive organic solvents and other polluting chemicals, they are slow and laborious, and the recovery of the components is seldom complete, **Gherasim, and Mikulášek, 2014**.

Membrane processes with different type of membranes give a good promise for removal of heavy metals for their space saving, easy operation and high efficiency. The membrane technologies utilized to remove heavy metals from the waste water are nanofiltration (NF), reverse osmosis (RO) and electrodialysis. NF is the intermediate system between ultrafiltration



and RO. Nanofiltration is a promising process for the retention of heavy metal ions such as, chromium, arsenic and copper from waste water. Nanofiltration membrane benefits from high efficiency of contaminant removal, comparatively low energy consumption, reliability and ease of operation, **Fu, and Wang, 2011**. In reverse osmosis, a pressure driven membrane, heavy metals is rejected, while water can pass through the membrane. Reverse osmosis membrane has been developed with a pore size down to 10^{-4} μm because of the stringent environmental legislation. Reverse osmosis membrane is more efficient for the removal of heavy metals from inorganic solution compared to nanofiltration, as indicated by the rejection percentage of over 97% with a concentration of heavy metals ranging from 21 to 200 ppm. The advantages of utilizing reverse osmosis involve a high salt rejection, high water flux, chemical stability, mechanical strength, the ability to withstand high temperatures and resistance to biological attack, **Kurniawan, et al., 2006**.

Some researchers investigated the application of nanofiltration and reverse osmosis processes for the treatment of waste water containing heavy metals such as copper and cadmium ions. Synthetic wastewater containing Cd^{+2} and Cu^{+2} ions at different concentrations were prepared and subjected to treatment by reverse osmosis and nanofiltration membranes in the laboratory. The results showed that high removal efficiency of the heavy metals could be achieved by reverse osmosis membranes which are 98 and 99% for copper and cadmium. Nanofiltration was able for removal of more than 90% of the copper ions existing in the feed water. The results showed that the reverse osmosis membranes was able for treating wastewater with an initial concentration of 500 mg/l and decreasing the concentration of ion to about 3 mg/l (removal of 99.4%), while the average removal efficiency of nanofiltration membranes was 97%, **Abu Qdais, and Moussa, 2004**.

In this study, the effect of time, feed concentration, pressure, flow rate, temperature and pH on flux and permeate concentration have been studied for polyamide spiral wound NF and RO membranes to remove heavy metals from electroplating wastewater. The concentration of heavy metal ions was measured by an atomic absorption spectrometry.

2. THEORETICAL BACKGROUND

The flux of solvent, which is generally water through the membrane is linearly proportional to the pressure difference and osmotic pressure difference across the membrane, **Kucera, 2010**:

$$J_w = k_w (\Delta P - \Delta \pi) \quad (1)$$

Where: J_w is the flux of water ($\text{l/m}^2\cdot\text{h}$), k_w is the permeability coefficient of pure water ($\text{l/m}^2\cdot\text{h}\cdot\text{bar}$), ΔP is the applied pressure driving force (bar) and $\Delta \pi$ is the osmotic pressure of the solution (bar).

Solution osmotic pressure is related to its dissolved solute concentration and is predicted from Van't Hoff equation as:

$$\pi = (\varphi i R_g T C) / M.wt \quad (2)$$

Where: φ is the osmotic coefficient (dimensionless), i is the number of dissociated ions per molecule (Van't Hoff factor) (dimensionless), T is the temperature (K), R_g is the universal gas constant ($\text{l}\cdot\text{bar}/\text{mole}\cdot\text{K}$), C is the concentration of solute (mg/l) and $M.wt$ is the molecular weight of solute.



The Van't Hoff factor is inserted to express the deviation from ideal solution behavior that implicates finite volume occupied by molecules of solute and their mutual attraction as in Vander Waals attraction, **Khudair, 2011**.

By measuring the solute concentrations in feed solution (C_F) and also in permeate solution (C_P), the rejection is calculated as follows, **Gherasim, and Mikulášek, 2014**:

$$R\% = \left(1 - \frac{C_P}{C_F}\right) * 100\% \quad (3)$$

Where: R is the solute rejection (percentage), C_P is the concentration in permeate (mg/l) and C_F is the concentration in feed solution.

Recovery can be expressed as the volume of permeate divided by the initial volume of feed. This expression applied in batch concentrating mode. For the overall system, the expression is, **Absar, et al., 2008**:

$$Y\% = \frac{V_P}{V_F^0} * 100\% \quad (4)$$

Where: $Y\%$ is the recovery (percentage), V_P is the volume of permeate (l) and V_F^0 is the initial feed volume (l).

3. EXPERIMENTAL WORK

Four types of feed solutions were used for the membrane process zinc chloride ($ZnCl_2$), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) and chromic chloride ($CrCl_3 \cdot 6H_2O$). Synthetic wastewater containing the desired concentrations of Zn^{+2} , Cu^{+2} , Ni^{+2} and Cr^{+3} were prepared by dissolving the desired amount of $ZnCl_2$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$ in deionized water of 1-2 $\mu s/cm$ conductivity. Solution pH was adjusted to a desired value by adding 0.5 M citric acid ($C_6H_8O_7 \cdot H_2O$) or 1 M sodium hydroxide (NaOH) as required. The total feed solution volume was 8 liters. The chemical analysis of components is given in **Table 1**. The polyamide thin-film composite nanofiltration and reverse osmosis membranes were used in this work. The specifications of NF and RO membranes are given in **Table 2**. Schematic diagrams of lab-scale NF and RO system used in these experiments are shown in **Fig. 1**.

Feed solution was prepared in feed vessel by dissolving the heavy metal compounds in 8 liter of deionized water. Pressure gauge (0-10 bar) was used in the feed line to indicate the operating pressure, the feed solution drawn from the feed vessel by centrifugal pump (Model: 15 GR-18, Rated power: 150 W, Rated voltage: 220-240 V, Rated current: 0.58 A, Rated speed: 2860 r/min, Frequency: 50/60 Hz, Highest head: 15 m, Rated head: 10 m, Max. capacity: 25 l/min, Rated capacity: 10 l/min, Insulation class: B) then the solution is introduced into the spiral-wound nanofiltration or reverse osmosis element by means of a high pressure pump (Model: HF-6050, Max. outlet pressure: 125 psi, Open flow: 1.2 l/min, VOLTS: 24 VDC, AMPS: 0.26 A). The feed temperature was varied by submersible electrical coil (Rated power: 1000 W, Rated voltage: 220V). The feed flow rate was controlled by rotameter (Range: 10-100 l/h). The concentrate stream is recycled to the feed vessel and mixed with the vessel. The water flux was obtained by dividing the permeate volume by the product of effective area of membrane and time. The concentration of heavy metal ions was measured by an atomic absorption spectrometry (Buck 210/211, Variable Slit Band Width 2A, 7A & 20A, Dimensions: 40"L x 12"W x 12"H; Weight: 50 lbs, U.S.A., Perkin Elmer, Sr.Nr:1159 A). After recording the results, the solution was drained by a drain valve and the system was washed by deionized water. After

each replacement for inorganic component, the membrane must be clean. For the cleaning of metallic scales low solution pH is used. Cleaning steps:

- Preparing the cleaning solution and adjust the pH.
- Pumping the cleaning solution into NF or RO membranes.
- Recycling the cleaning solution.
- Cleaning the unit with deionized water. The cleaning continues until the conductivity of the product stream reaches approximately those of feed water.

4. RESULTS AND DISCUSSION

4.1 Effect of Operating Conditions

It can be easily observed from **Figs. 2** and **3** that the flux from nanofiltration and reverse osmosis unit decrease with increase in operating time. The continuous decline of the flux was mainly because of the gradual solution viscosity increment and to heavy metal deposition on the surface of the membrane; with the increasing in feed concentration and osmotic pressure gradually, which led to further membrane scaling and concentration polarization. Due to the boundary layer on the surface of the membrane formed by heavy metals the resistance against flux increased. This behavior is in agreement with **Lee, et al., 2006** and **Wang, et al., 2007**. For NF membrane the increase in time to 70 min resulted in the decline of flux from 20.667 to 15.405 LMH for zinc, 17 to 14.405 LMH for copper, 12.333 to 11.44 LMH for nickel and 17 to 13.667 LMH for chromium. For RO membrane the increase in time to 70 min resulted in the decline of flux from 11.083 to 10.393 LMH for zinc, 10.583 to 9.655 LMH for copper, 9.083 to 8.798 LMH for nickel and 10.333 to 9.238 LMH for chromium. **Figs. 4** and **5** show the effects of time on recovery percentage of permeate. The recovery percentage increased according to Eq. (4) because the accumulation volume of permeate has been increased as time increased. For NF the increase in time to 70 min resulted in the increase of water recovery from 9.25 to 60.06% for nickel, 12.75 to 71.75% for chromium, 12.75 to 75.62% for copper and 15.5 to 80.87% for zinc. For RO the increase in time to 70 min resulted in the increase of water recovery from 6.81 to 46.18% for nickel, 7.75 to 48.5% for chromium, 7.93 to 50.68% for copper and 8.31 to 54.56% for zinc. **Figs. 6** and **7** show that the heavy metal ions concentration in the product gradually increased with increase in operating time. This behavior can be explained by the increase of the feed concentration with time in the recirculation mode led to increase in concentration polarization and this cause an increase in the salt passage. This behavior is in agreement with **Wei, et al., 2013** (who studied the changes in the chromium, copper, and nickel ion concentrations in the permeate and rejection rates versus operating time under a continuous concentration process, respectively). Over the course of operation, the heavy metal concentrations in permeate gradually increased. The heavy-metal concentrations in permeate only slightly increased with continued operation). For NF membrane the first 30 minutes resulted in the increase in permeate concentration of 42.79% for zinc, 66.31% for copper, 15.49% for nickel and 33.29% for chromium. The final 40 minutes resulted in the increase in permeate concentration of 26.05% for zinc, 95.17% for copper, 43.96% for nickel and 127.27% for chromium. For RO membrane the first 30 minutes resulted in the increase in permeate concentration of 17.72% for zinc, 70.37% for copper, 54.77% for nickel and 66.72% for chromium. The final 40 minutes resulted in the increase in permeate concentration of 52.58% for zinc, 18.43% for copper, 41.35% for nickel and 14.59% for chromium. The behavior of rejection of heavy metal ions as shown in **Figs. 8** and **9** due to the concentration of heavy metal ions in permeate which has increased with time and the increase in feed concentration (feed concentration has been changed with time) because of the recirculation mode. The rejection at first three minutes when the feed concentration approximately constant for chromium in NF and

RO was 99.7% and 99.93%, for copper was 98.43% and 99.33%, for zinc was 97.96% and 99.49%, for nickel was 97.18% and 99.49% respectively.

Fig. 10 shows that the permeate flux have been decreased with increasing feed concentration of zinc. This behavior is due to increase in osmotic pressure, decrease of the effective pore size of the membrane due to adsorption of solute on the surface of the membrane and the effect of concentration polarization. This behavior is in agreement with **Al-Rashdi, et al., 2013**. The possibility of fouling inside the pores of membrane would be larger in case of the concentrated solution flowing, this fouling could act in blockage a number of bores completely or partly, so the flux would be decreased. The increase in feed concentration of zinc ions from 10 to 300 mg/l resulted in the decline in flux of 24.7% for NF and 20.48% for RO. **Fig. 11** shows that zinc ions concentration in permeate has been increased as the feed concentration increased due to the increase in concentration of feed due to recirculation mode. This behavior is in agreement with **Ahn, et al., 1999**. The increase in feed concentration of zinc ions from 10 to 300 mg/l resulted in the increase of permeate concentration from 1.409 to 13.71 mg/l for NF and 0.19 to 4.63 mg/l for RO.

Fig. 12 shows the permeate flux has been increased with increasing applied pressure, this behavior is due to an increase of the preferential sorption of water at higher pressure, and thus the solvent permeability increases at high pressure compared with the solute permeability. This behavior is in agreement with **Lee, et al., 2006**. The increase in applied pressure from 1 to 4 bar resulted in the increase in flux of 304.06% for NF and 311.98% for RO. **Fig. 13** shows the concentration of zinc ions in permeate has been decreased with increasing applied pressure which can be explained by the following: at low pressure the solute diffusive transport through the membrane is higher than that of convective transport. As the applied pressure increases, the decrease of the concentration of ions in permeate becomes possible due to convective transport becomes more important at high pressure. This behavior was observed for RO membrane, this behavior is in agreement with **Chai, et al., 1997**. For NF membrane the permeate concentration has been decreased and then increased at high pressures, this behavior can be explained as the increase in pressure caused an increase in the flux so that the solution level in the feed tank decreased and the feed became more concentrated (i.e. the concentration of zinc ions in feed solution is higher than that of initial feed concentration) and the concentration polarization has been increased with increasing pressure causing an increase in permeate concentration at high pressures, in this case the effect of both concentration polarization and convective transport play an important role. This behavior is in agreement with **Al-Rashdi, et al., 2013**. The permeate concentration had decreased from 20.85 to 11.01 mg/l at $p=1-3$ bar and then increased to 11.45 mg/l at $p=4$ bar for NF and decreased from 6.89 to 3.45 mg/l for RO.

Fig. 14 shows that the permeate flux increases with increasing in feed flow rate (cross flow velocity). These increment means that there is a boundary layer concentration polarization at the surface of the membrane, as the flow rate or cross flow velocity has been increased this boundary layer has been decreased. This behavior is I agreement with **Murthy, and Chaudhari, 2009**. The increase in feed flow rate from 20 to 50 l/h resulted in the increase in flux of 6.25% for NF and 5.48% for RO. **Fig. 15** shows that the increase in feed flow rate leads to a decrease in the permeate concentration of nickel ions. Similar behavior were found in literature **Frare`s, et al., 2005 and Ahn, et al., 1999**. Mass transfer coefficient increased with increase in feed flow rate which decreased the concentration polarization and decrease the permeate concentration and this behavior is in agreement with **Gherasim, and Mikulášek, 2014, Boricha, and Murthy, 2009 and Murthy, and Chaudhari, 2009**. The increase in feed flow rate from 20 to 50 l/h resulted in the decrease of permeate concentration of 7.13% for NF and 38.27% for RO.

It is clear from **Fig. 16** that the increase in feed temperature leads to an increase in permeates flux. This behavior can be explained as the solvent diffusion coefficient increased, the average pore size of the active layer increased slightly and the solution viscosity decreased with an increase in the temperature of feed, which led to an increase in the permeate flux. This behavior is in agreement with **Wei, et al., 2013 and Wang, et al., 2007**. The increase in feed temperature from 26 to 40 °C resulted in the increase in flux of 9.64% for NF and 55% for RO. **Fig. 17** shows that the increases in feed temperature leads to an increase in permeate concentration of copper ions. Increasing the temperature influence the heavy metals adsorption by the membranes, more copper ions will be adsorbed on the membrane surface due to the diffusion rate of the molecules has been increased, also the increase of membrane pore size resulting in an increase in the permeate concentration. This behavior is in agreement with **Abd Alameer, 2011**. The increase in feed temperature from 26 to 40 °C resulted in the increase of permeate concentration of 8.28% for NF and 6.14% for RO.

It is clear from **Fig. 18** that for chromium the flux has been decreased as the pH goes from the acidic side towards the alkaline side. More decrease is shown around the region of pH=5 and pH=7 for NF membrane and at pH=7 for RO membrane. The maximum flux of chromium was at pH=4 for both membrane. It is well known that when the pH of the solution decreases, the solubility of dissolved salts increases. From membrane point of view, this would decrease the rate of fouling on the membrane surface which leads to decrease the osmotic pressure and consequently the permeate flux would increase. On the contrary increasing pH of solution would accelerate the deposition of salt on membrane surface. This agrees with **Abd Alameer, 2011**. **Fig. 19** shows that the increase in pH would lead to an increase in the precipitation of dissolved salts which will foul the membrane surface, hence, increasing the resistance to salt passage through the membrane. Therefore higher removal values are obtained at pH=7 for chromium. The decreasing of pH means the increasing of the concentration of hydrogen ion, H^+ , while the increasing of pH is a result of increasing of hydroxide ion OH^- . The molecular weight of hydroxide ion is much larger than H^+ . According to the pore side theory for membranes the permeation of hydrogen ion with small molecular weight (i.e. small ions size) is larger than the hydroxide ion, and this can be explain the reason of the high permeability of heavy metal ions in lower pH range. The electrical charge equilibrium will be varied according to the concentration of the ions on both sides of the membrane. This behavior agrees with **Al-Alawy, 2000**.

The flux for nanofiltration is higher than that from reverse osmosis membrane; this is due to the pore size of nanofiltration membrane which is larger than that of reverse osmosis membrane and the RO has higher osmotic pressure than NF membranes as a result the permeability of pure water for nanofiltration is approximately twice that of RO. The flux of NF is higher than that of RO for chromium about 50-82%, copper 30-62%, nickel 22-36% and zinc 50-85%. The concentrations of heavy metal ions in permeate for nanofiltration is higher than that from reverse osmosis membranes. The concentration or rejection has been affected by size exclusion than other mechanisms, and NF has higher MWCO which means larger pore size than RO, but rejection for RO system mainly depends on solution diffusion transport.

4.2 NF and RO Simulated Electroplating Wastewater

Experiments has been made to show the effect of time (0-70 min) on the flux and concentration of heavy metal ions in NF and RO process for a mixture of synthetic electroplating wastewater, **Wei, et al., 2013**. **Figs. 20 to 22** show the effect of time for a mixture of electroplating wastewater on flux and the concentration of heavy metal ions in permeate for NF and RO. The increase in time to 70 min resulted in the decline of flux from 16.83 to 13.48 LMH for NF process and 10.17 to 9.32 LMH for RO process. The increase in time to 70 minutes



resulted in the increase in permeate concentration for NF process from 0.042 to 0.568 mg/l for zinc, 1.878 to 7.01 mg/l for copper, 0.696 to 2.654 mg/l for nickel and 0.421 to 2.461 mg/l for chromium. The NF membrane has allowed permeation of chromium, nickel, copper and zinc ions to lower than permissible limits. For RO process the permeate concentration has been increased from 0.0335 to 0.12 mg/l for zinc, 0.848 to 2.442 mg/l for copper, 0.541 to 0.807 mg/l for nickel and 0.13 to 0.643 mg/l for chromium. The RO membrane has allowed permeation of chromium, nickel, copper and zinc ions to lower than permissible limits. The explanation for this behavior for NF and RO is the same as explained in section 4.1.

5. CONCLUSIONS

Nanofiltration and reverse osmosis processes can be used for recovery of water from heavy metal solutions. The polyamide nanofiltration membrane has allowed permeation of chromium and copper ions to lower than permissible limits. Nanofiltration membrane has allowed permeation of nickel and zinc ions at low concentration of these ions. The polyamide reverse osmosis membrane gives a high efficiency for removal of chromium, copper, nickel and zinc ions and it has allowed permeation of these ions to the lower than permissible limits. The rejection at first three minutes when the feed concentration approximately constant for chromium in NF and RO was 99.7% and 99.93%, for copper was 98.43% and 99.33%, for zinc was 97.96% and 99.49%, for nickel was 97.18% and 99.49% respectively. The maximum recovery for chromium in NF and RO was 71.75% and 48.5%, for copper was 75.62% and 50.68%, for zinc was 80.87% and 54.56%, for nickel was 60.06% and 46.18% respectively. For a mixture of synthetic electroplating wastewater, nanofiltration and reverse osmosis membranes have a high rejection percentage for heavy metal ions. Pure water was obtained and with concentration of less than the allowed for heavy metals in the case of the mixture.

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NOMENCLATURE

C	concentration of solute, mg/l
C_F	concentration in feed solution, mg/l
C_P	concentration in permeate, mg/l
i	number of dissociated ions per molecule (Van't Hoff factor), dimensionless
J_w	flux of water, l/m ² .h



k_w	permeability coefficient of pure water, $l/m^2 \cdot h \cdot bar$
Q_F	feed flow rate, l/h
R	solute rejection, percentage
R_g	universal gas constant, l.bar/mole.K
T	temperature, K
t	time, min
V_F^o	initial feed volume, l
V_p	volume of permeate, l
Y	recovery, percentage
ΔP	applied pressure driving force, bar
$\Delta \pi$	osmotic pressure of the solution, bar
φ	osmotic coefficient, dimensionless

ABBREVIATIONS

NF	Nanofiltration
UF	Ultrafiltration
RO	Reverse osmosis
LMH	Liter per square meter per hour
MWCO	Molecular weight cut off

Table 1. Chemical specification of inorganic compounds.

Specification	Zinc Chloride ($ZnCl_2$)	Copper Chloride Dihydrate ($CuCl_2 \cdot 2H_2O$)	Nickel Chloride Hexahydrate ($NiCl_2 \cdot 6H_2O$)	Chromic Chloride ($CrCl_3 \cdot 6H_2O$)
Minimum assay	97.0%	99.0%	98.0%	97.0%
Molecular weight	136.28	170.48	237.69	266.45
CAS-No.	7646-85-7	10125-13-0	13478-00-7	10078
Made in	India	India	India	England

Table 2. Specification of nanofiltration and reverse osmosis element.

Specifications	NF	RO
Type of membrane	Polyamide thin-film composite	Ultra low pressure aromatic polyamide reverse osmosis membrane element
Active membrane area, m^2	0.36	0.36
Average permeated flow	$0.57 m^3/d$	$0.19 m^3/d$
Maximum feed water SDI	5	5
Maximum feed water temperature $^{\circ}C$.	45	45
pH range of feed water during continuous operation	2-11	3-10
pH range of feed water during chemical cleaning	1-12	2-12

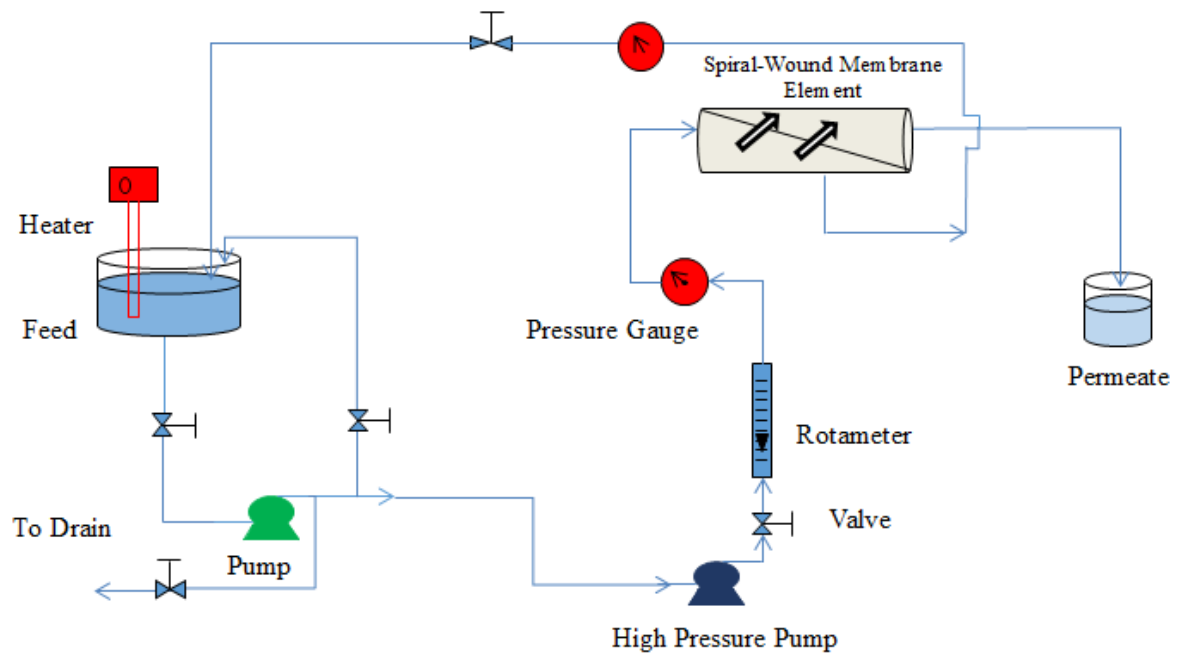


Figure 1. Schematic diagram of lab-scale RO system.

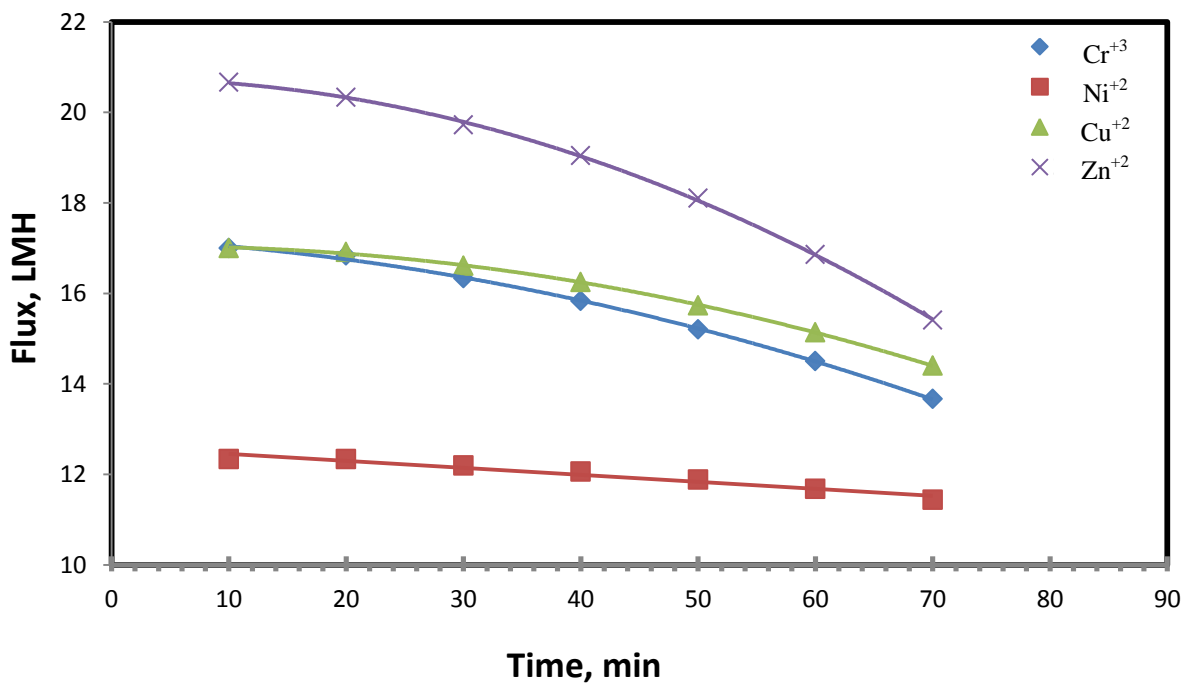


Figure 2. Effect of operating time on flux for NF process ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $C_{F, \text{ions}}=300$ mg/l).

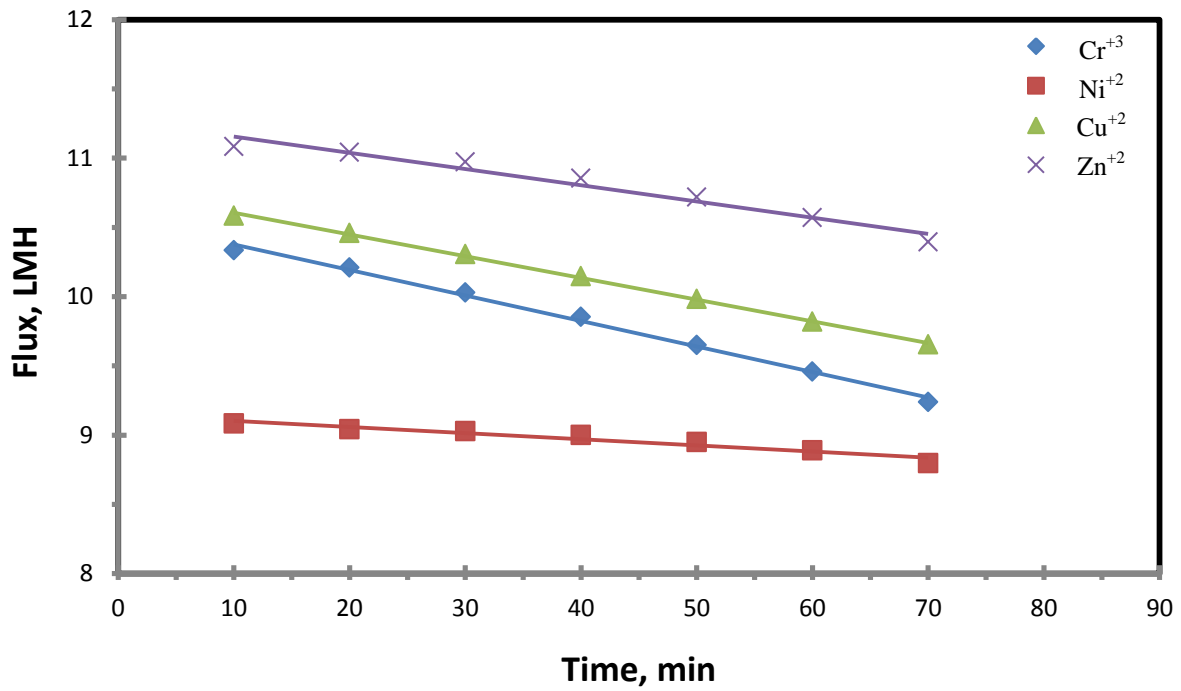


Figure 3. Effect of operating time on flux for RO process ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $C_{F, ions}=300$ mg/l).

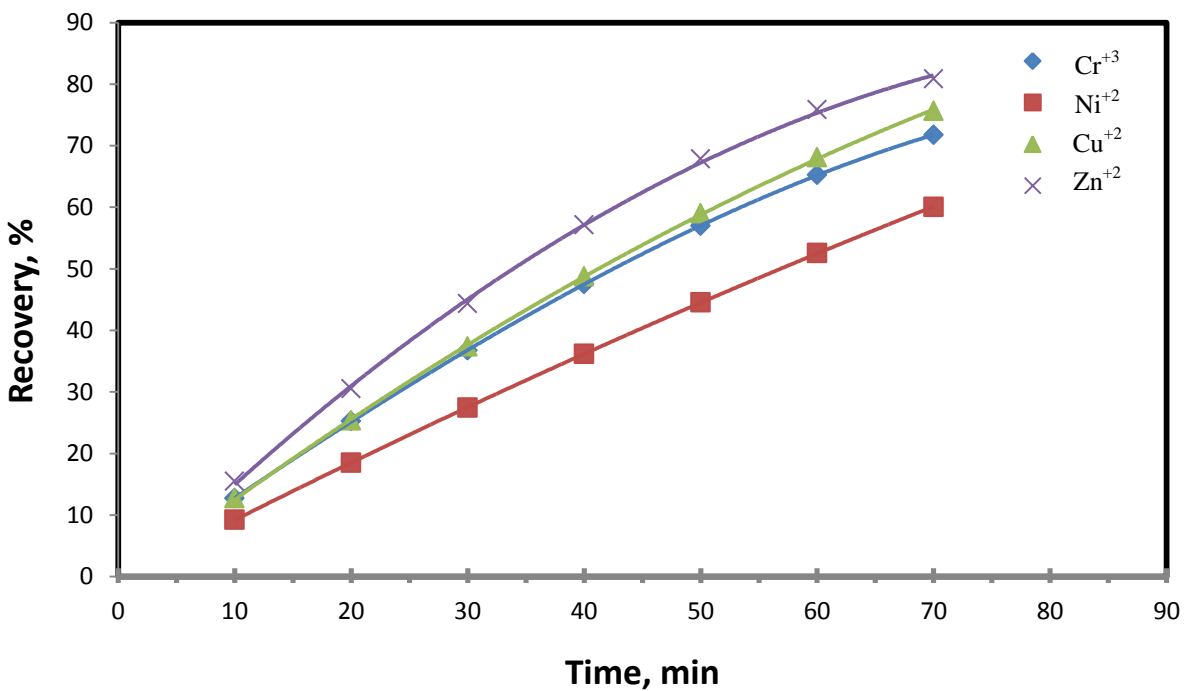


Figure 4. Effect of operating time on recovery percentage for NF process ($Q_F = 40$ l/h, $T = 26$ °C, $P = 2$ bar, $C_{F, ions}=300$ mg/l).

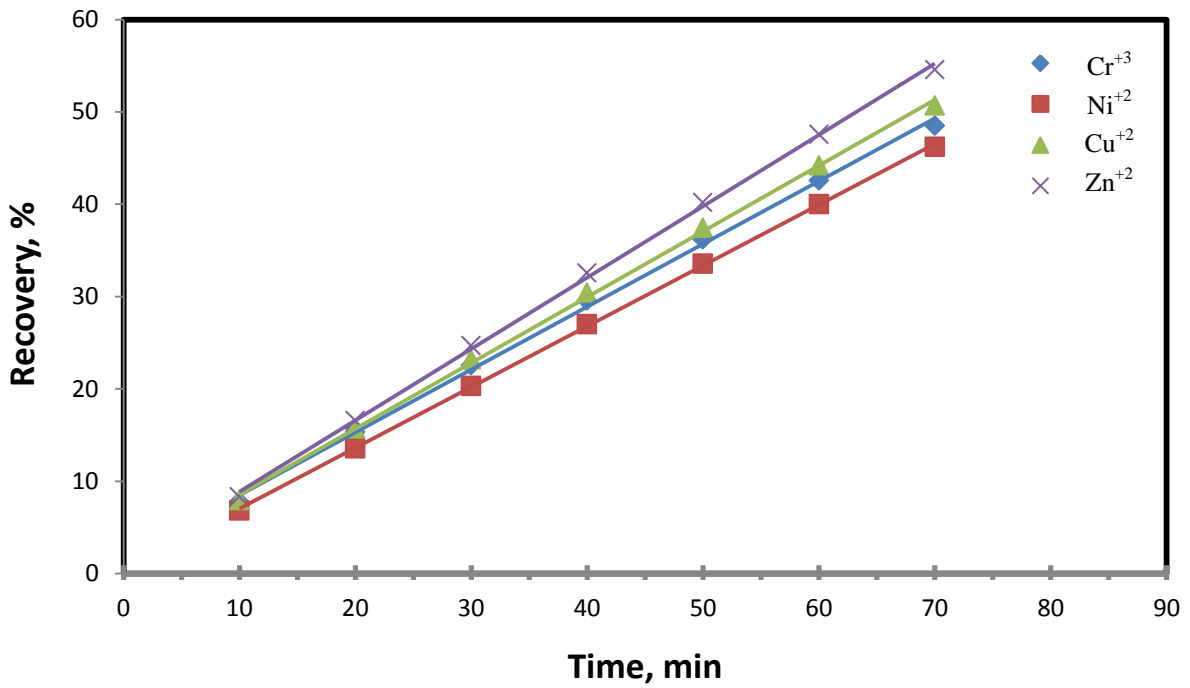


Figure 5. Effect of operating time on recovery percentage for RO process ($Q_F = 40$ l/h, $T = 26$ °C, $P = 2$ bar, $C_{F, ions} = 300$ mg/l).

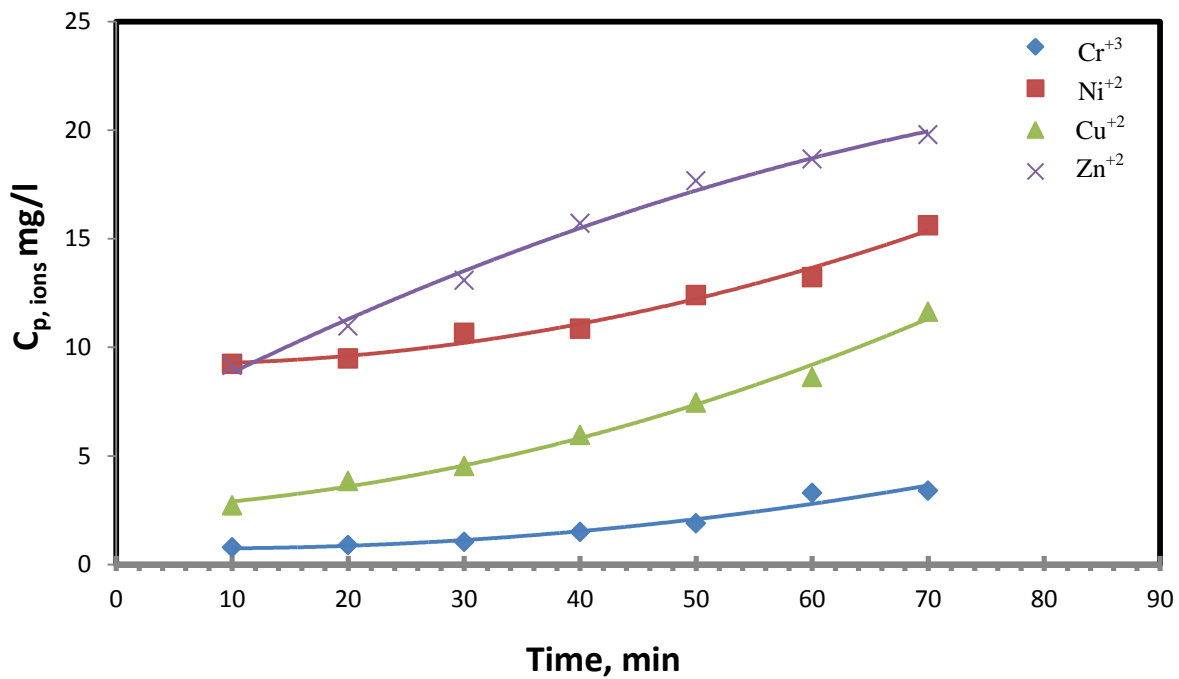


Figure 6. Effect of operating time on permeate concentration of ions for NF process ($Q_F = 40$ l/h, $T = 26$ °C, $P = 2$ bar, $C_{F, ions} = 300$ mg/l).

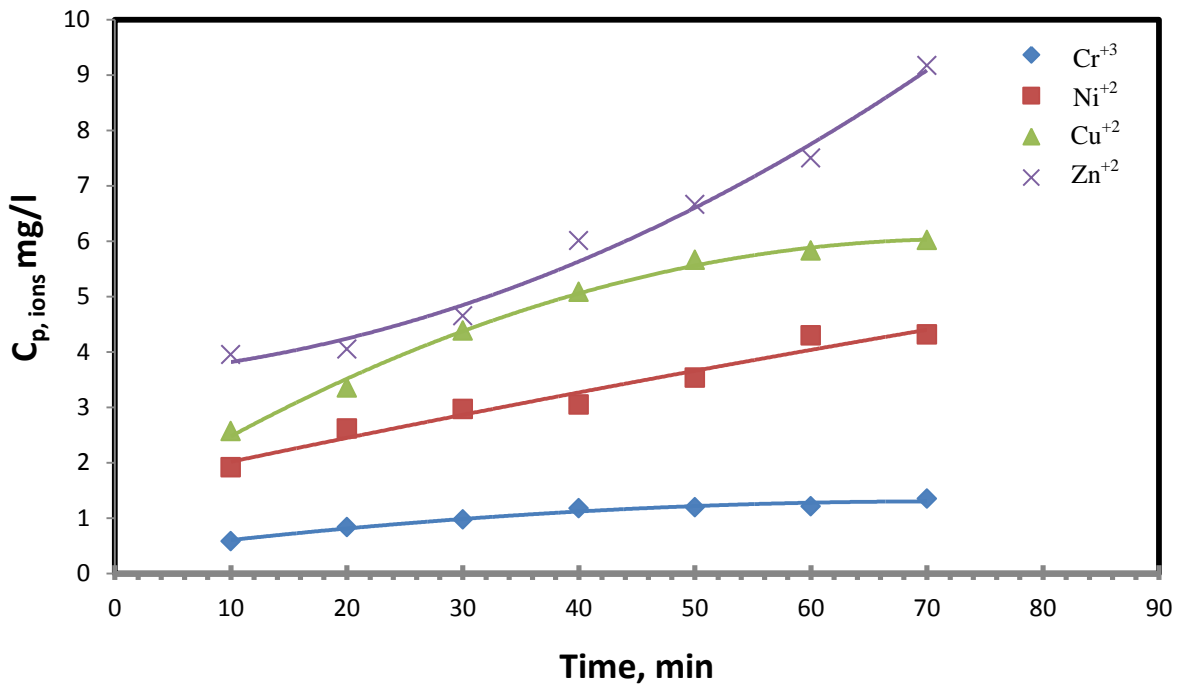


Figure 7. Effect of operating time on permeate concentration of ions for RO process ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $C_{F, ions}=300$ mg/l).

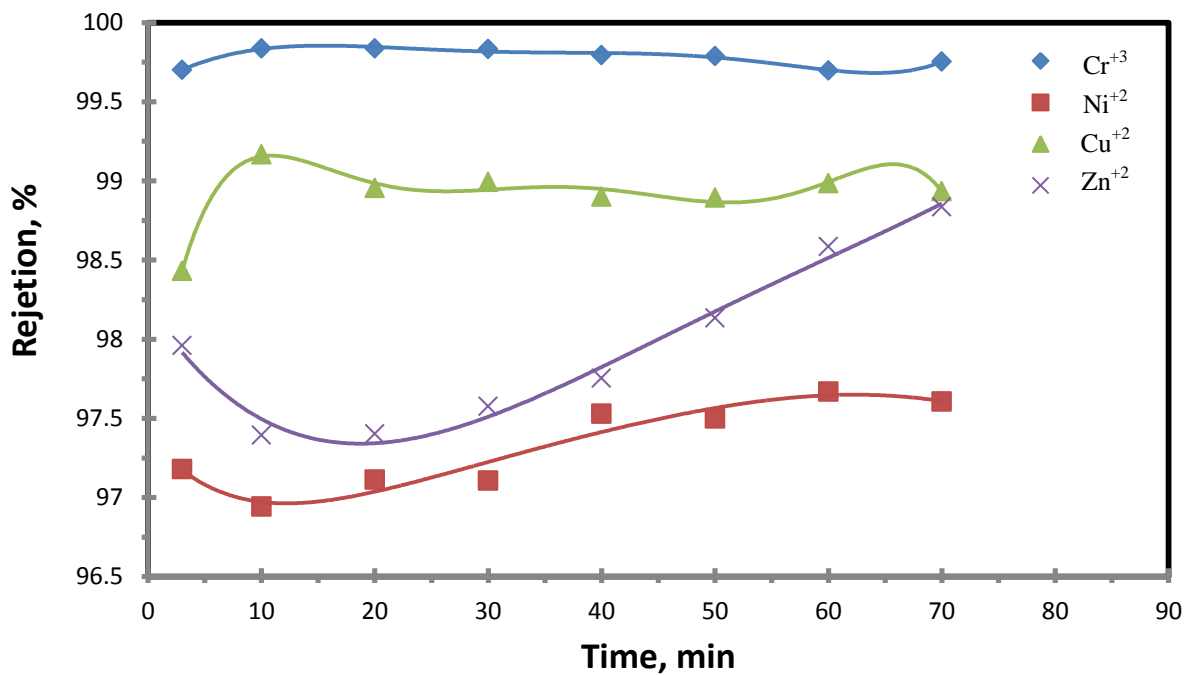


Figure 8. Effect of operating time on rejection percentage of heavy metal ions for NF process ($Q_F = 40$ l/h, $T = 26$ °C, $P = 2$ bar, $C_{F, ions}=300$ mg/l).

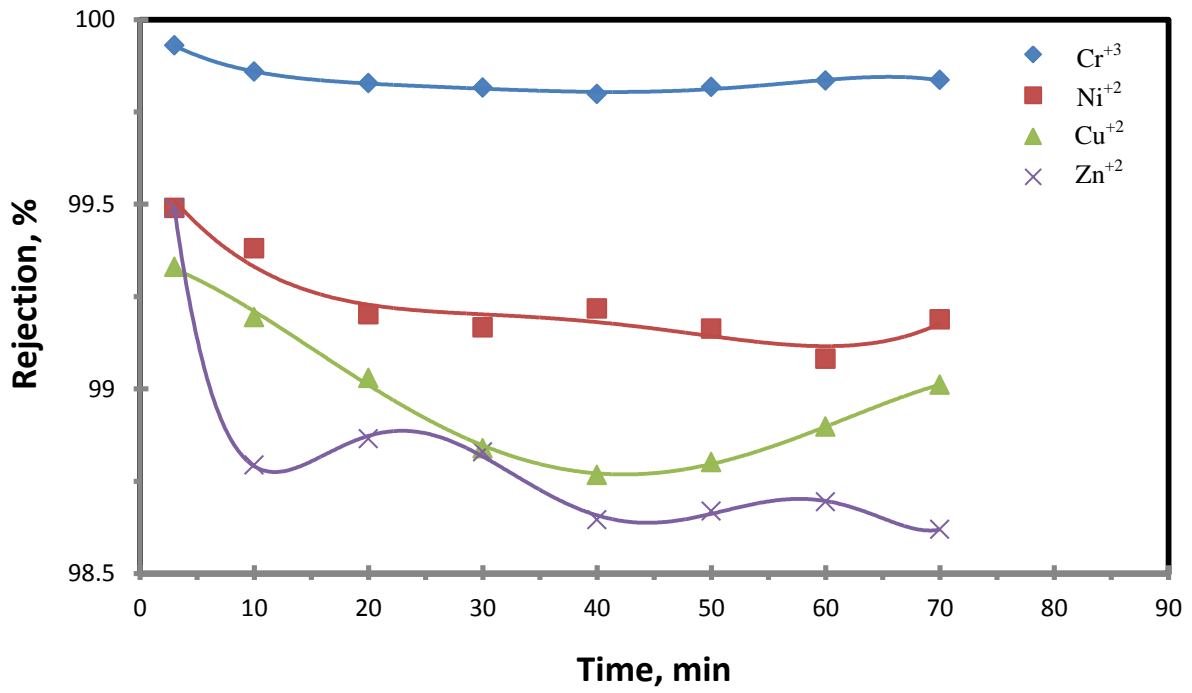


Figure 9. Effect of operating time on rejection percentage of heavy metal ions for RO process ($Q_F = 40$ l/h, $T = 26^\circ\text{C}$, $P = 2$ bar, $C_{F, \text{ions}} = 300$ mg/l).

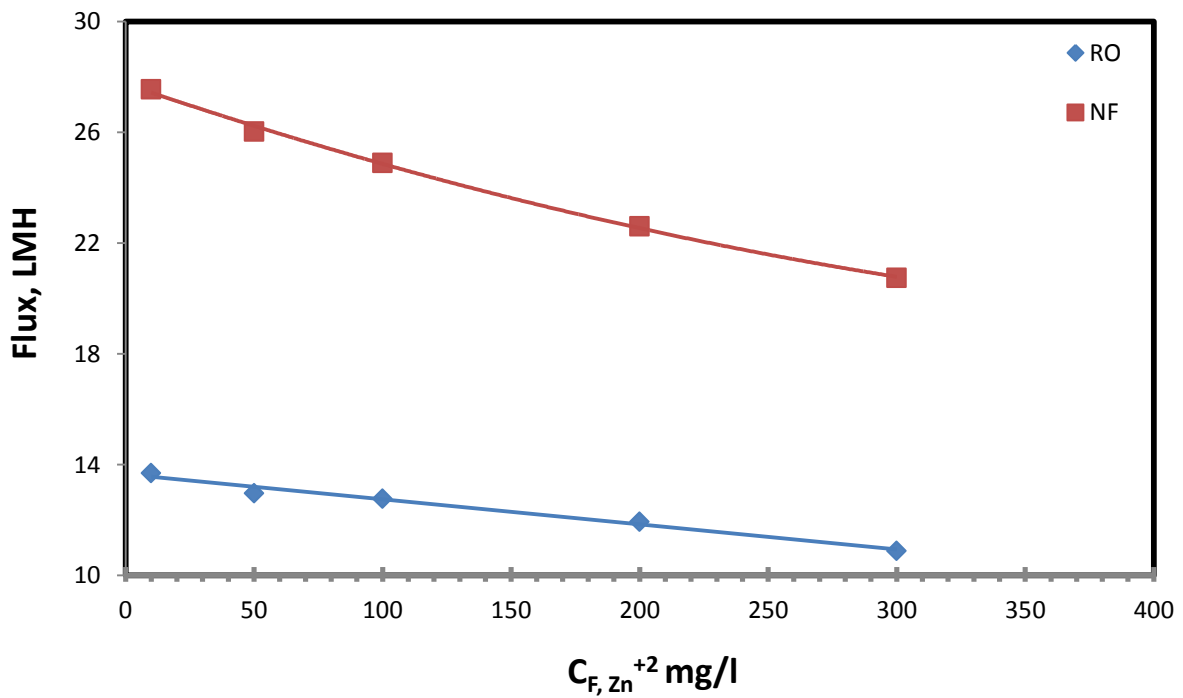


Figure 10. Effect of feed concentration of zinc ions on flux ($t = 30$ min, $T = 26^\circ\text{C}$, $P = 2$ bar, $Q_F = 40$ l/h, $\text{pH} = 6$).

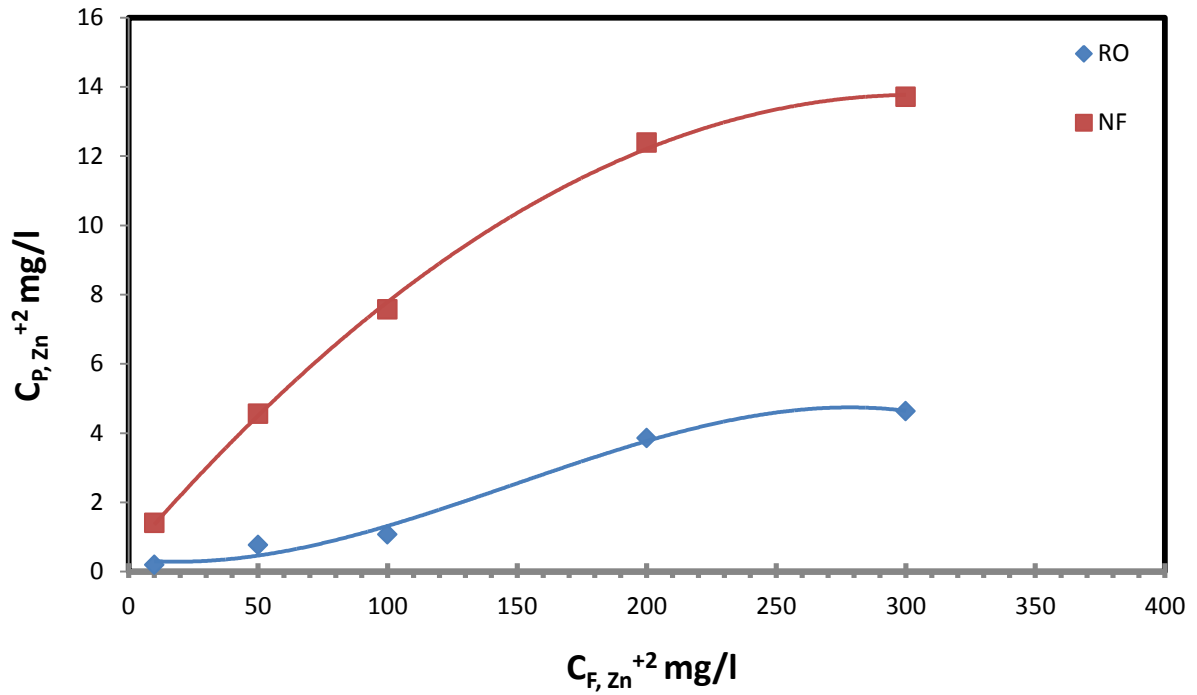


Figure 11. Effect of feed concentration of zinc ions on permeate concentration ($t=30$ min, $T=26$ °C, $P=2$ bar, $Q_F=40$ l/h, $pH=6$).

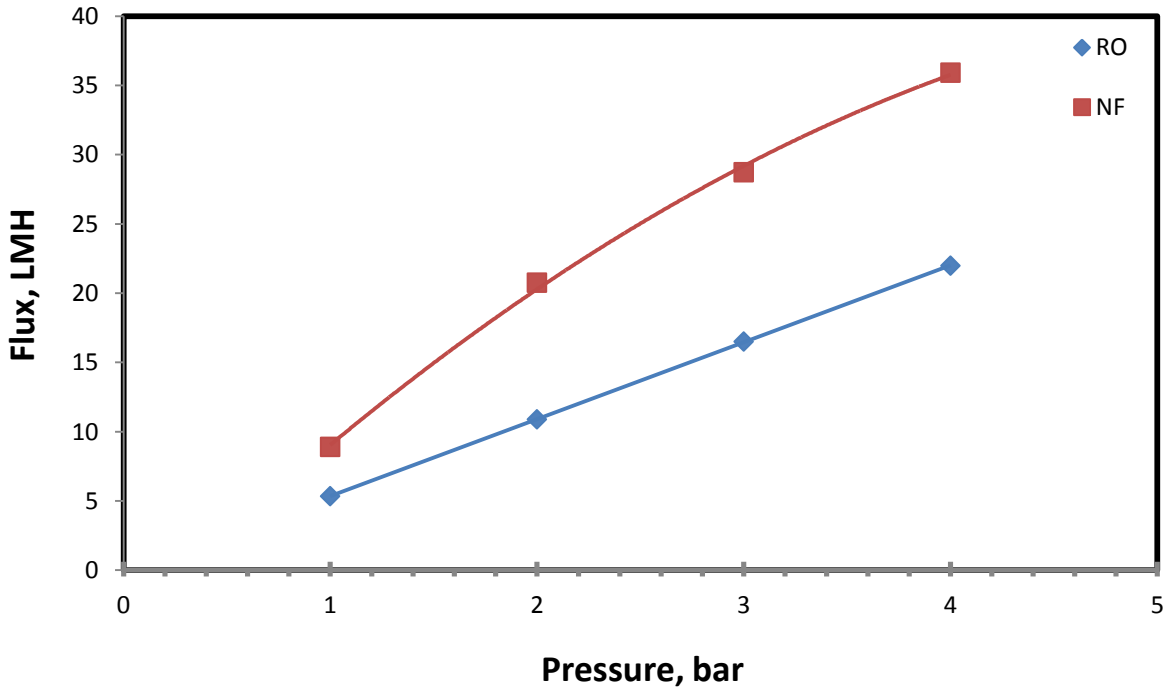


Figure 12. Effect of operating pressure on flux for zinc ions ($t=30$ min, $T=26$ °C, $Q_F=40$ l/h, $C_{F,Zn^{+2}}=300$ mg/l, $pH=6$).

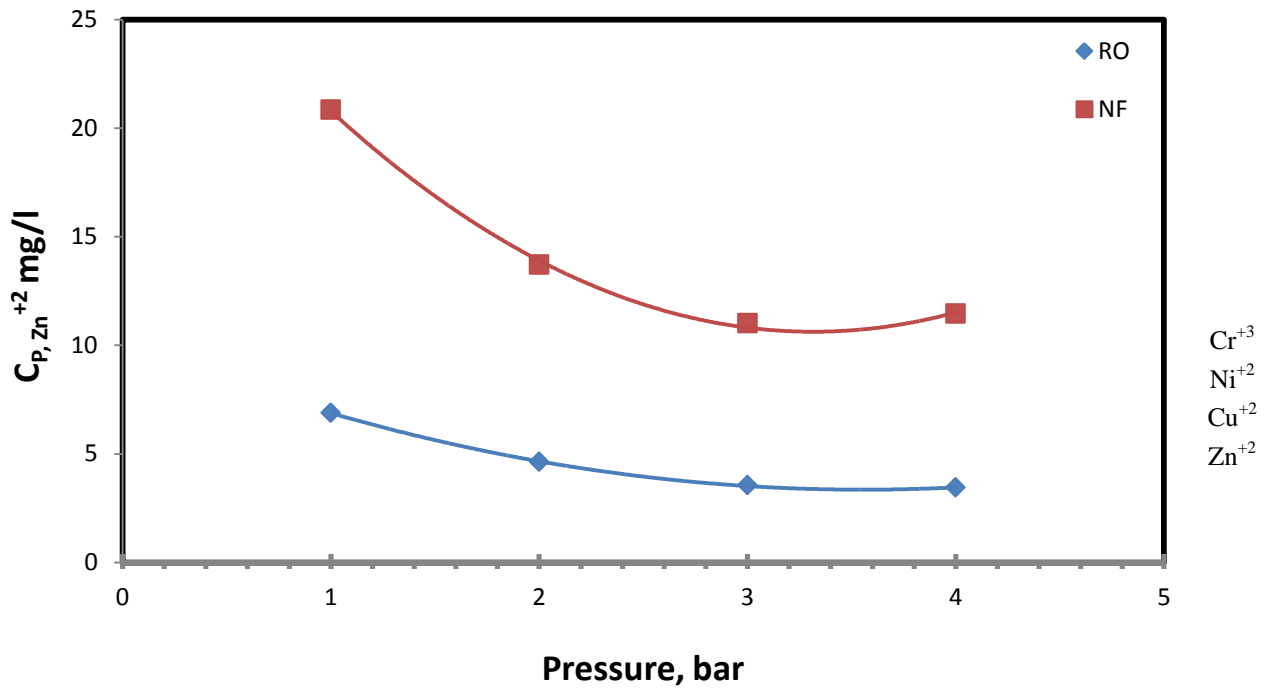


Figure 13. Effect of operating pressure on permeate concentration of zinc ions ($t=30$ min, $T=26$ °C, $Q_F=40$ l/h, $C_{F, Zn^{+2}}=300$ mg/l, $pH=6$).

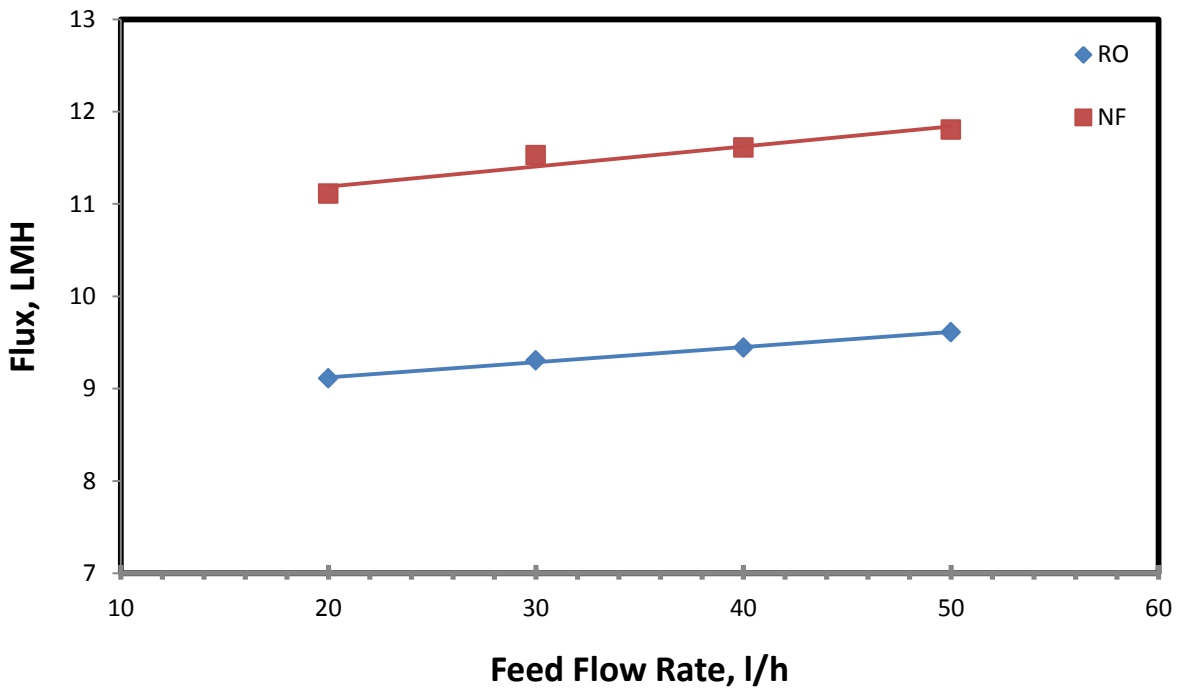


Figure 14. Effect of feed flow rate on flux for nickel ions ($t=30$ min, $T=26$ °C, $P=2$ bar, $C_{F, Ni^{+2}}=300$ mg/l, $pH=6$).

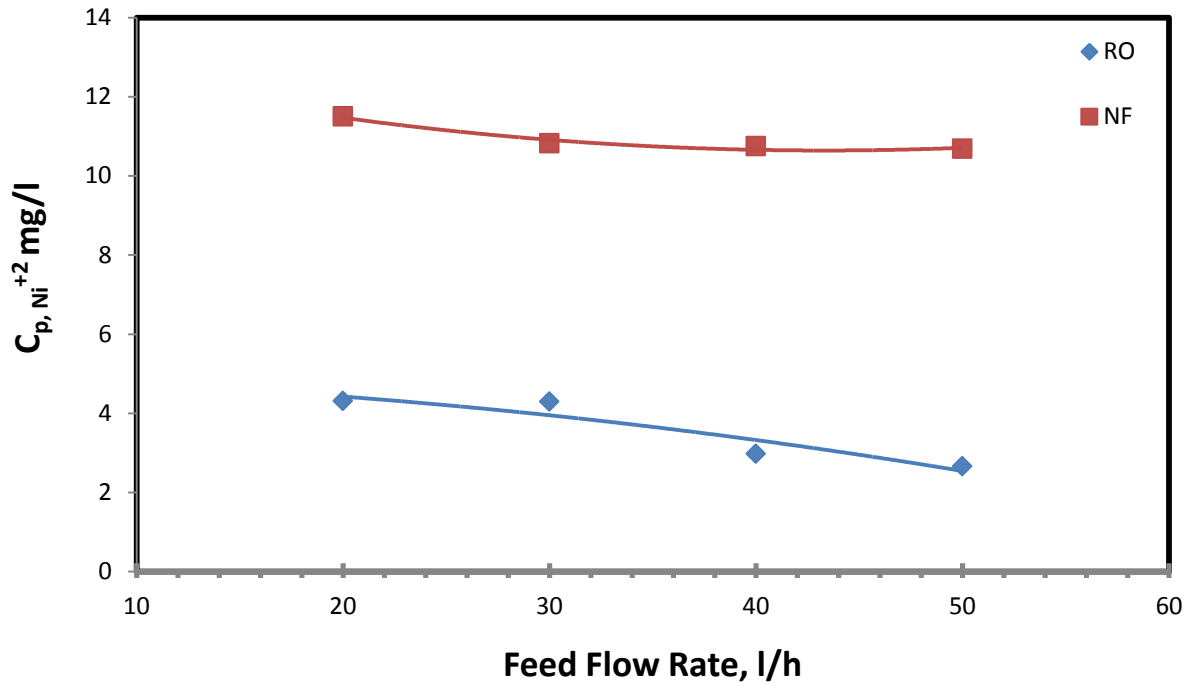


Figure 15. Effect of feed flow rate on permeate concentration of nickel ions ($t=30$ min, $T=26$ °C, $P=2$ bar, $C_{F, Ni^{+2}}=300$ mg/l, $pH=6$).

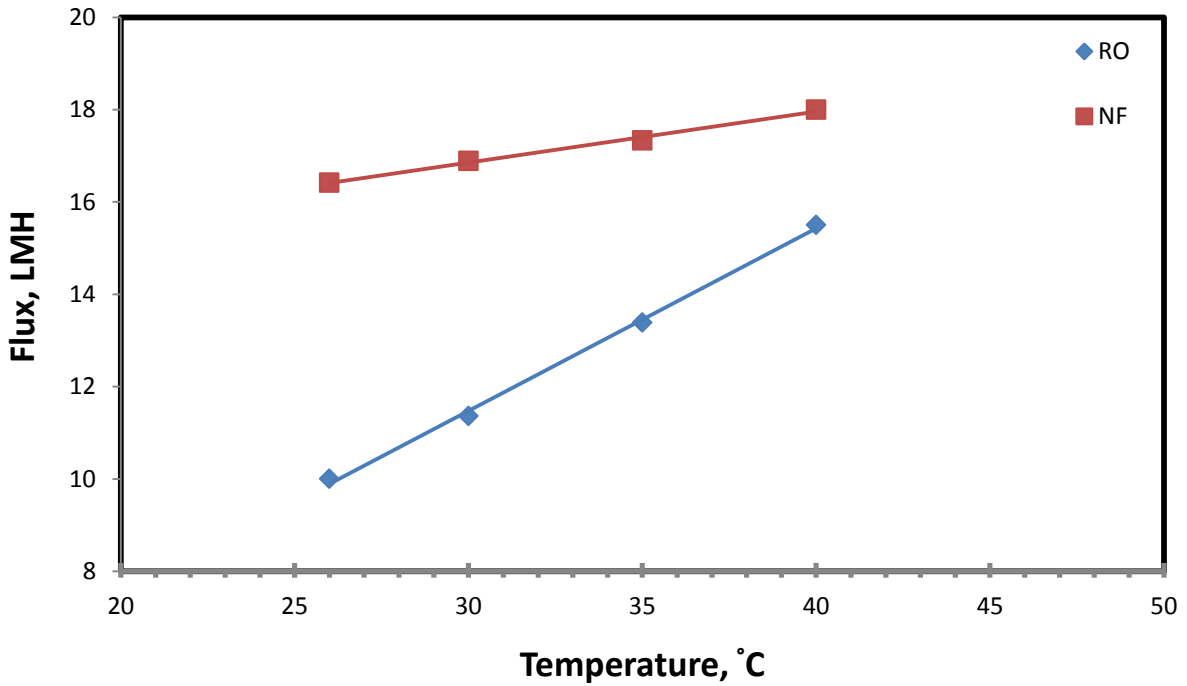


Figure 16. Effect of feed temperature on flux for copper ions ($t=30$ min, $P=2$ bar, $Q_F=40$ l/h, $C_{F, Cu^{+2}}=300$ mg/l, $pH=5$).

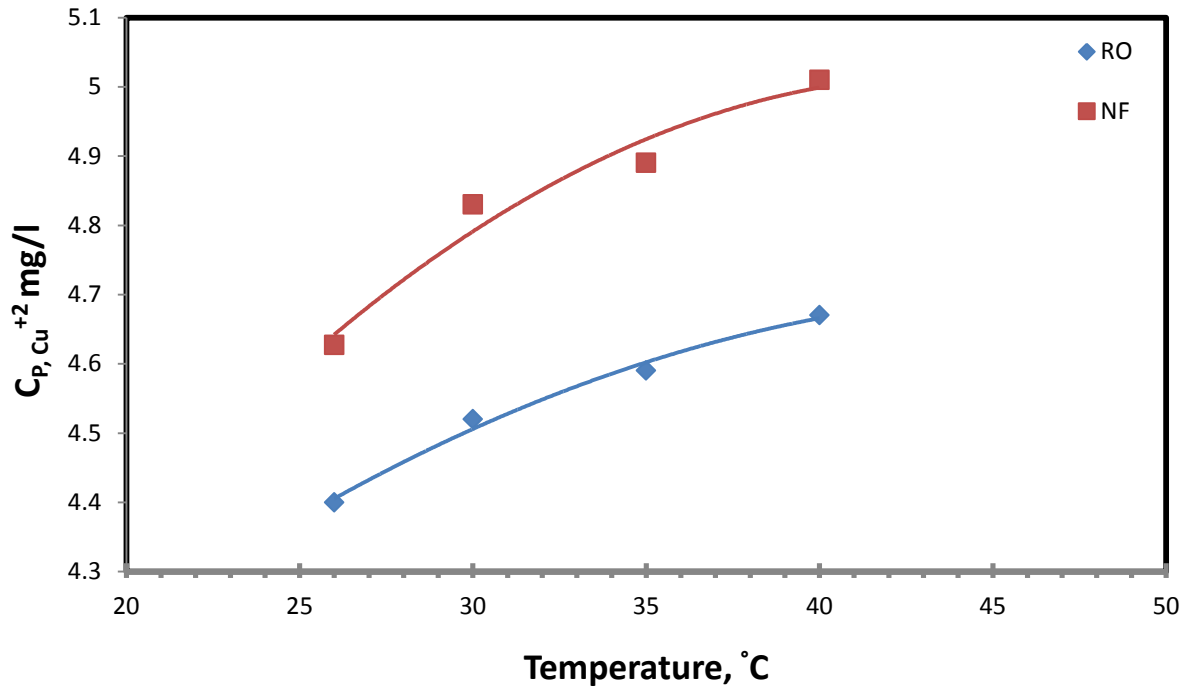


Figure 17. Effect of feed temperature on permeate concentration of copper ions ($t=30$ min, $P=2$ bar, $Q_F=40$ l/h, $C_{F, Cu^{+2}}=300$ mg/l, $pH=5$).

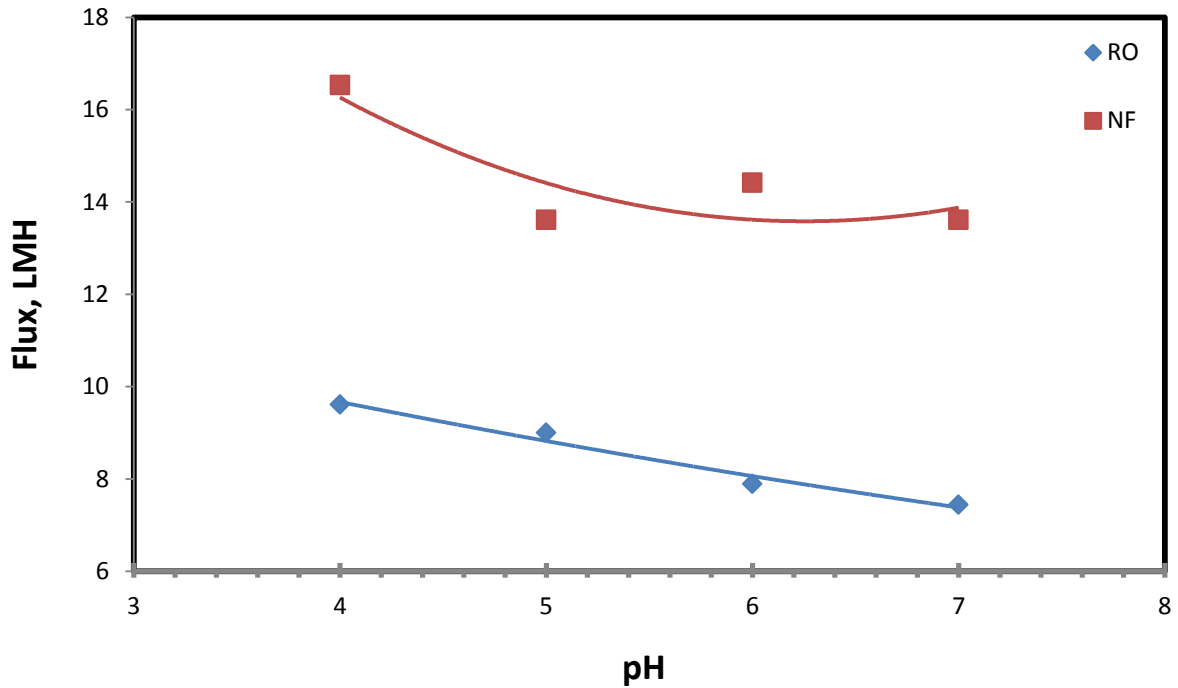


Figure 18. Effect of feed pH on flux for chromium ions ($t=30$ min, $T=26$ °C, $P=2$ bar, $C_{F, Cr^{+3}}=300$ mg/l, $Q_F=40$ l/h).

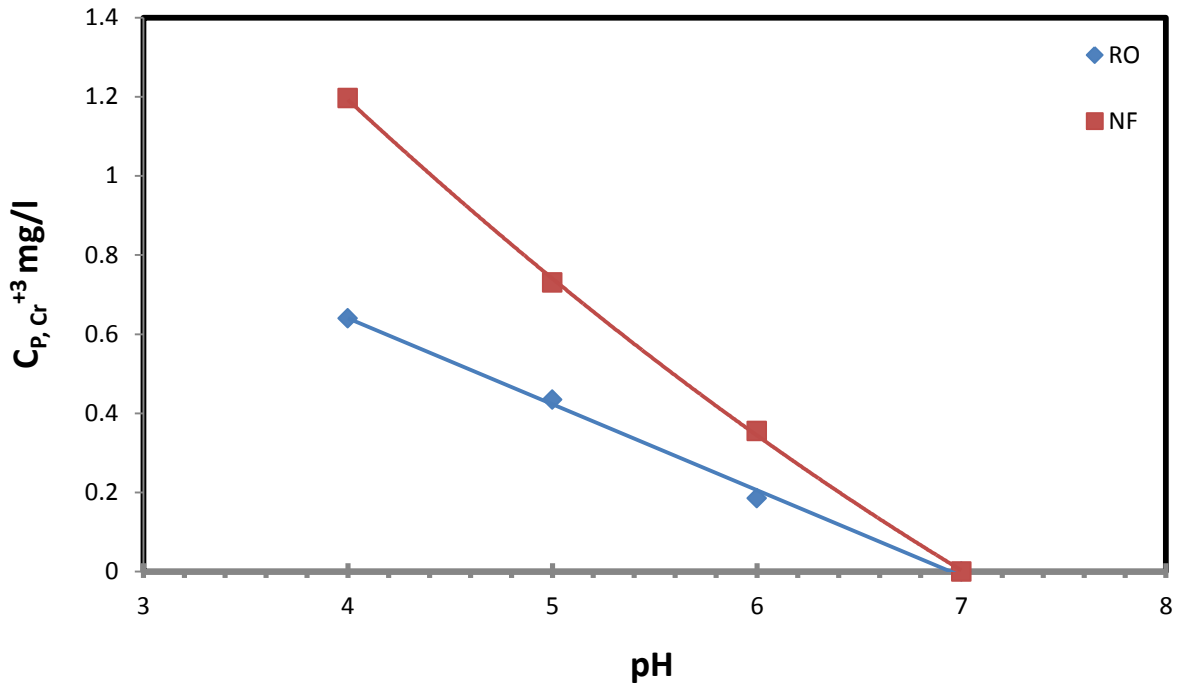


Figure 19. Effect of feed pH on permeate concentration of chromium ions ($t=30$ min, $T=26$ °C, $P=2$ bar, $C_{F,Cr^{+3}}=300$ mg/l, $Q_F=40$ l/h).

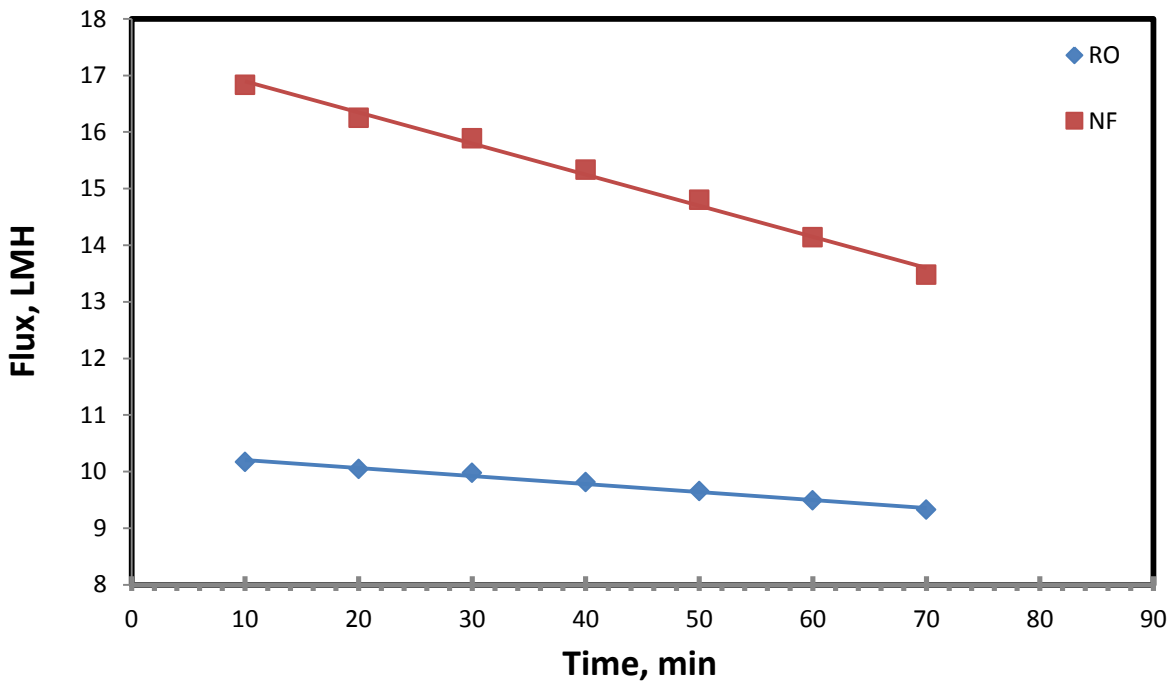


Figure 20. Effect of operating time on flux of a mixture of electroplating wastewater ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $pH=3.49$, $C_{F,Zn^{+2}}=15$ mg/l, $C_{F,Cu^{+2}}=60$ mg/l, $C_{F,Cr^{+3}}=125$ mg/l, $C_{F,Ni^{+2}}=150$ mg/l).

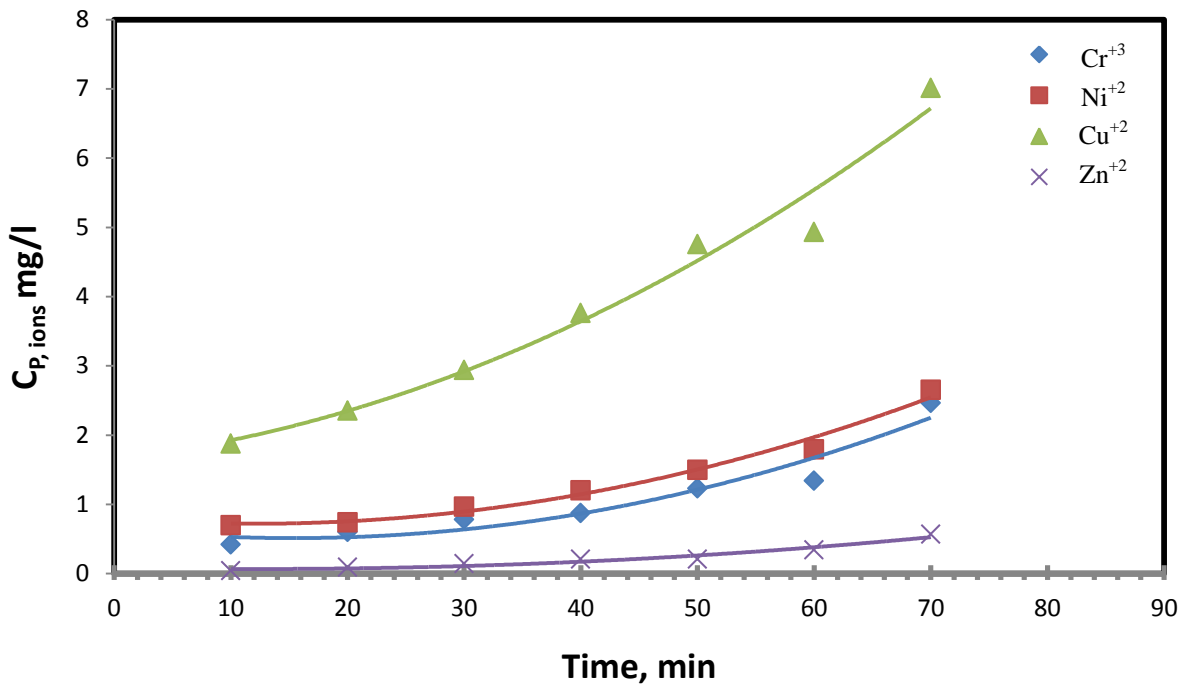


Figure 21. Effect of operating time on permeate concentration of ions in a mixture of electroplating wastewater for NF process ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $pH=3.49$, $C_{F, Zn^{+2}}=15$ mg/l, $C_{F, Cu^{+2}}=60$ mg/l, $C_{F, Cr^{+3}}=125$ mg/l, $C_{F, Ni^{+2}}=150$ mg/l).

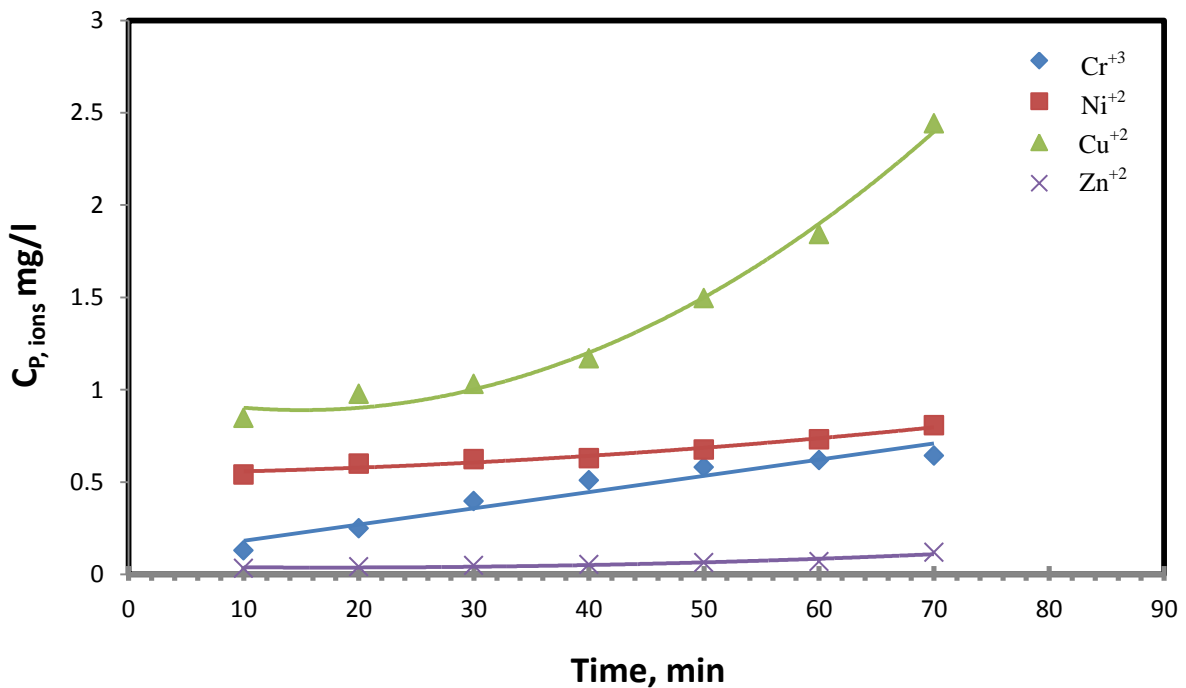


Figure 22. Effect of operating time on permeate concentration of ions in a mixture of electroplating wastewater for RO process ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $pH=3.49$, $C_{F, Zn^{+2}}=15$ mg/l, $C_{F, Cu^{+2}}=60$ mg/l, $C_{F, Cr^{+3}}=125$ mg/l, $C_{F, Ni^{+2}}=150$ mg/l).